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Solvent effect on H-bond cooperativity factors in ternary complexes of methanol, octan-1-ol, 2,2,2-trifluoroethanol with some bases

Boris N. Solomonov *, Mikhail A. Varfolomeev, Dilyara I. Abaidullina

Chemical Institute, Kazan State University, Kremlevskaya 18, Kazan 420008, Russia

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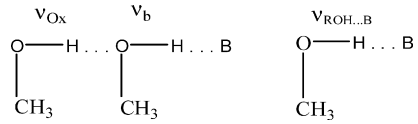
Abstract

Cooperative hydrogen bonds in ternary complexes $(ROH)_2\cdots B$ (ROH—alcohols; B—bases) formed in pure bases (B) and solutions in *n*-hexan carbon tetrachloride, benzene and 1,2-dichloroethane were studied by FTIR spectroscopy. Based on the observations, the authors were able propose an original method of evaluating solvent effects on cooperativity factors in the complexes. Frequencies of cooperative hydrogen bon $OH\cdots B$ (ν_b) were determined for ternary complexes of pyridine with aliphatic alcohols (methanol, octan-1-ol) and for 2,2,2-trifluoroethanol w three different bases (acetonitrile, diethyl ether, tetrahydrofuran). The solvent shifts of ν_b were found to correlate with an empirical thermochemi parameter of the solvent, S_{VW}. The cooperativity factors were determined for the complexes $(ROH)_2\cdots B$ in all studied media. It has been found th the cooperativity factors are almost independent of the solvent. In addition, a method was proposed of estimating the frequencies and cooperativ factors for ternary complexes $(ROH)_2\cdots B$ in the gas phase. It has been found that in gas phase the cooperativity factors are practically the sa as in condensed media.

Keywords: Solvent effect; Cooperativity; Hydrogen bonding; FTIR spectroscopy; Gas phase

1. Introduction

Formation of hydrogen bonds (HB) plays a dominant role in many chemical and biological processes [1,2]. Hydrogen bond is regarded as non-covalent type of interaction, and one of its basic properties is non-additivity or cooperativity [1–4]. The phenomenon of HB cooperativity is important in a variety of molecular recognition processes, in stabilization of folded proteins and in non-covalent synthesis [5–13]. The concept of cooperativity between two or more hydrogen bonds implies that the primary H-bond formed between proton donor X-H and proton acceptor B (X-H···B), becomes stronger when a third partner Y-H or X-H forms another hydrogen bond with a lone pair of atom X (Y-H···X-H···B or X-H···X-H···B) [2,14–22]. The most pure systems that hydrogen bond cooperativity takes place are aliphatic alcohols. There are a large number of works devoted to studying cooperative hydrogen bond in these systems. But only few of them contain quantitative parameters of cooperative hydrogen bond determined by experimental methods. Kleeberg et al. [18–20] have proposed to evaluate the cooper tivity by using factors A_b and A_{Ox}, which can be obtained fro the plots of the experimental frequencies ν_b and ν_{Ox} again $\nu_{X\text{-}H\cdots B}$. The meaning of the vibrational frequencies ν_b, ν and $\nu_{X\text{-}H\cdots B}$ is explained in the scheme below (for a terna complex $(CH_3OH)_2\cdots B$).



Recently in Ref. [23] a new method of evaluating the coo erativity factors in complexes $ROH\cdots O(R)H\cdots B$ has be proposed. In Ref. [23], the cooperativity factors A_b and A for complexes $(CH_3OH)_2\cdots B$ were defined by the followi equations:

$$A_b = \frac{\nu_{free}^{OH} - \nu_b^{(CH_3OH)_2\cdots B}}{\nu_{free}^{OH} - \nu^{CH_3OH\cdots B}}, \quad (1$$

$$A_{Ox} = \frac{\nu_{free}^{OH} - \nu_{Ox}^{CH_3OH\cdots O(CH_3)H\cdots}}{\nu_{free}^{OH} - \nu^{CH_3OH\cdots O(CH_3)H}}, \quad (1$$

* Corresponding author. Tel.: +7 843 2315346; fax: +7 843 2315346.
E-mail address: Boris.Solomonov@ksu.ru (B.N. Solomonov).

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